NATIONAL BUREAU OF STANDARDS REPORT

7547

Progress Report

on

Metallurgical Considerations in the Design of Plastic Gallium Alloys Which Harden at Room Temperature

by

Richard M. Waterstrat

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS

Metallurgical Considerations in the Design of Plastic Gallium Alloys Which Harden at Room Temperature

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Abstract

An experimental approach is used to obtain information on the alloying behavior of gallium when it is mixed with various pure metal powders at room temperature and the mixture is allowed to harden. The experimental observations indicate that the metals which produce hardening at room temperature are largely concentrated in or near group VIII in the periodic table. Tentative explanations for some of the observed effects are given.

1. INTRODUCTION

There has been some recent interest in the development of gallium alloys which may be plastically shaped after their initial preparation and which subsequently harden at room temperature (1, 2, 3, 4, 10).

Plastic amalgams which harden at room temperature have been in use for many years as dental restorative materials. The alloy commonly used is prepared by mechanically mixing a powdered silver-tin alloy (Ag_3Sn) together with liquid mercury in a mortor and pestle or in a mechanical amalgamator. The mixture remains plastic for several minutes at room temperature and during this time may be molded or carved to any desired shape. The alloy will subsequently harden by a process involving a chemical reaction between the alloy powder and the liquid mercury resulting in the formation of intermediate phases having high strength and hardness. As the liquid mercury is consumed in this reaction the alloy loses its plasticity and becomes rigid due to the formation of the solid intermediate phases in the interstices between the original powder particles.

The mechanism of this hardening reaction is not well understood but it is known to involve isothermal difussion and a chemical reaction between the solid and liquid components. Hardening may occur at room temperature providing that one of the metallic components remains a liquid at this temperature. The only metals besides mercury which are liquids within a few degrees of room temperature are cesium and gallium, which melt at 29.7° C and 29.8° C respectively. The chemical reactivity of cesium rules out any extensive use of this metal but gallium metal is especially attractive owing to its tendencies to wet many materials and to form intermediate phases with other metals (5). The development of gallium alloys is retarded, however, by the lack of basic information relating to the metallurgy of these alloys and it is the purpose of this report to provide some information concerning the alloying behavior of gallium at room temperature.

In selecting a suitable base metal for the solid alloy powder, one should probably eliminate from consderation as engineering materials, those metals which are either poisonous or extremely reactive. In addition the alloy system selected must contain an intermediate phase, since this hardening reaction will not occur in simple eutectic systems such as gallium with zinc, tin or indium. By applying these

limiting rules to combinations of gallium with the various metallic elements in the periodic table, one finds that the choice of a base metal will be restricted to one of the transition elements or an element of the copper-silver-gold triad (Figure 1).

These metals all form intermediate phases with gallium at elevated temperatures and the highly exothermic reactions involved indicate that the phases formed are quite stable. However, since the reaction rate decreases exponentially with temperature, according to the Arrhenius equation, it is not surprising that there is no observable reaction at room temperature in some of these systems. The presence of an oxide film on the metal would also act as a powerful barrier to atomic diffusion at room temperature and consequently metals such as chromium might not react perceptibly with gallium at room temperature even though a strong reaction occurs at higher temperatures (1). The kinetics of the hardening reaction therefore apparently vary appreciably among the different alloy systems at room temperature and an experimental approach is necessary in determining which of these metals will produce a hardening reaction when mixed with liquid gallium.

2. EXPERIMENTAL PROCEDURE

Since the melting point of pure gallium is slightly above room temperature it is necessary to use a eutectic alloy of gallium in order to prepare these mixtures at room temperature. A gallium eutectic alloy containing 11% tin was selected which has a melting point of 20° C. The addition of 11% tin has been shown not to appreciably affect the hardening reaction although it does seem to have some effect in retarding it (2). The experimental alloys were therefore allowed to harden for one month before they were examined by X-ray diffraction in order to detect the presence of any intermediate phases. The presence of these phases would indicate that a reaction had occurred. The metal powders were obtained from various commercial sources and were at least 99.6% pure in all cases. They were passed through a 325 mesh sieve before mixing them with the gallium eutectic alloy in a glass mortor and pestle. The powders all appeared to be quite dry and clean prior to mixing and therefore no attempt was made to clean or dehydrate them.

The optimum time of mixing and the pressure exerted varies with the different systems and no attempt was made to standardize the mixing conditions. Each metal was mixed with sufficient liquid alloy to give a "wet" mixture and the excess liquid was then expressed by squeezing the alloy in a clean cloth before packing it into standard steel molds 4mm diameter by 8 mm long. The percentage of liquid present in the alloy after packing in the steel mold was estimated at between 20% and 40%. After removal from the mold the alloys were allowed to harden in air.

The techniques employed here are believed to be satisfactory for a preliminary survey since the object of this investigation was to determine whether each metal would harden or react with gallium at room temperature. The X-ray diffraction data were obtained using a General Electric XRD-5 diffractometer.

3. RESULTS AND DISCUSSION

The results of this investigation are given in Table 1. It may be noted that the metals which produce hardening at room temperature are largely concentrated in or near group VIII in the periodic table (Figure 1). One might be tempted to speculate that in order to obtain alloys which harden the metal powder should have a face-centered cubic structure. However, an iron-manganese alloy ($Fe_{0.6}Mn_{0.4}$) having the face-centered cubic structure did not harden or react with the liquid gallium eutectic. Reactions did occur with vanadium which has a body-centered cubic crystal structure and with magnesium which has a hexagonal crystal structure. It therefore seems unlikely that the crystal structure of the metal powder has any significant influence in determining which metals will harden. In general, metals with high melting points such as iridium, tantalum, and tungsten could be expected to react more slowly than metals with a lower melting point since the rate of diffusion at room temperature may be related to the binding energy in the solid phase. A high melting temperature implies a strong bonding and consequently a more sluggish reaction. The iridium alloy required many hours before hardening. The lack of hardening in tungsten or tantalum alloys might be attributed solely to this effect although it is possible that in all cases where hardening did not occur it may be the result

of a combined effect of low atomic mobility as well as the presence of an oxide film on the metal powders. The metals which hardened satisfactorily are all known to be relatively free of stable surface oxide films except for copper, and it was found that for this metal satisfactory hardening was not obtained unless the copper powder had been recently deoxidized by heating to 400° C in a hydrogen atomosphere (4). In most cases the intermediate phases forming were not identified. The crystal structures occurring in the gallium-gold and gallium-copper alloys however were identified as $AuGa_2$ and $CuGa_2$ respectively. These binary systems have been adequately investigated (6) and the crystal structures of the intermediate phases are known. In each case the phase formed initially is the one richest in gallium. In the silver-mercury system the phase which is formed during hardening (Ag_2Hg_3) is the one richest in mercury and it may be significant that at room temperature the intermediate phases which form during these hardening reactions are in each case the ones richest in the liquid component. When alloy powders consisting of copper-gold solid solutions were reacted with liquid gallium eutectic alloy it was found that both $AuGa_2$ and $CuGa_2$ phases were formed in amounts roughly proportional to the copper-gold ratio.

In certain cases violent exothermic reactions occur at room temperature when mixing these alloys. When very fine powders are mixed and condensed into volumes of about 0.5 cc sufficient heat may be evolved to raise the temperature of the mixture to its melting point (1).

Violent exothermic reactions at room temperature occurred in gallium-gold and gallium-palladium alloys but in both cases the reactions could be prevented by using a large excess (approximately 2:1) of liquid during mixing and subsequently expressing the excess liquid using a squeeze cloth before packing the mixture into the steel mold. It is also advisable to cut the plastic mass into smaller pieces before packing them in the mold and to use a mortor and pestle which have been cooled below room temperature in a refrigerator. When these precautions are taken there is very little temperature rise and small quantities of the gallium-gold alloys have been used in certain special applications without any difficulties (3, 10). The exothermic reactions can also be retarded by using a coarser powder or by dissolving another metal into the palladium or gold which would serve to dilute the pure metal.

Although silver powder reacts readily with the gallium eutectic, the mixtures either do not harden or are rather weak. An examination of the silver-gallium phase diagram (6) leads to a tentative explanation for this observation. It may be noted that the only well-substantiated intermediate phase is the one rich in silver. The existence of another phase is questionable. The X-ray pattern of the silver-gallium alloy showed the lines of a phase having a hexagonal crystal structure. If this phase is indeed the one rich in silver (ζ') then only 20% gallium would be required for its complete formation and any excess of gallium would result in a permanently soft, plastic mixture. On the other hand a gallium content of less than 20% may not be enough to produce a sufficient volume of the ζ' phase or to obtain the most desirable microstructure in these heterogeneous alloys. It appears therefore that in systems where the only intermediate phase is one which has a high percentage of the solid metal component the hardening will not be pronounced and may not occur at all even though a chemical reaction between the liquid and solid phases does occur as shown by X-ray diffraction data.

The alloys described here may have applications in dentistry as a restorative material and may be superior in many ways to ordinary dental amalgam (1, 7, 8, 9). They may also be used as a cold-solder for attaching electrical leads (3, 4, 10) and could find use in ceramic to metal seals It is hoped that this preliminary description of the alloying behavior of gallium will help to stimulate further research on this unusual metal.

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TABLE 1

Alloy*	Reaction After 1 Month		X-ray Pattern	Comments
	Hardens	Does Not Harden		
Ga_E+Mg	X		No lines were observed	Alloy slowly decomposes in air at room temperature
Ga_E+Ti		X	No lines were observed	Forms a black powder
Ga_E+V	X			
Ga_E+Cr		X	Cr	Exothermic reaction occurs at higher temperatures
Ga_E+Mn		X	αMn	Exothermic reaction occurs when the mixture is heated
Ga_E+Fe		X	Fe	Exothermic reaction occurs when the mixture is heated
Ga_E+Co	X		αCo+?	
Ga_E+Ni	X		Ni+?	Exothermic reaction occurs when the mixture is heated
Ga_E+Cu	X		Cu+$CuGa_2$	Cu powder must be deoxidized in order to produce a complete reaction
Ga_E+Zr		X	No lines were observed	
Ga_E+Nb		X	Nb	Exothermic reaction occurs when the mixture is heated
Ga_E+Mo		X	Mo	Exothermic reaction occurs when the mixture is heated

TABLE 1 (Con't.)

Alloy*	Reaction After 1 Month		X-ray Pattern	Comments
	Hardens	Does Not Harden		
Ga_E+Ru		X	Ru	Exothermic reaction occurs when the mixture is heated
Ga_E+Rh	X		Rh+?	
Ga_E+Pd	X		Pd+?	Exothermic reaction occurs at room temperature
Ga_E+Ag		X	Hexagonal phase	This phase may be the ζ' phase of ref. 5
Ga_E+Ta		X	Ta	
Ga_E+W		X	W	
Ga_E+Os		X	Os	
Ga_E+Ir	X		Ir+?	Exothermic reaction occurs when the mixture is heated, hardens slowly
Ga_E+Pt	X		Pt+?	Exothermic reaction occurs when the mixture is heated
Ga_E+Au	X		Au+$AuGa_2$	Exothermic reaction occurs at room temperature
Ga_E+Au (heated to 296°C)	X		AuGa	Au+$AuGa_2$→AuGa reaction begins at about 100° C
Ga_E+ (80%Au20%Cu)	X		F.C.C.†+$AuGa_2$+ $CuGa_2$	
Ga_E+ (50%Au50%Cu)	X		F.C.C.†+$AuGa_2$+ $CuGa_2$	

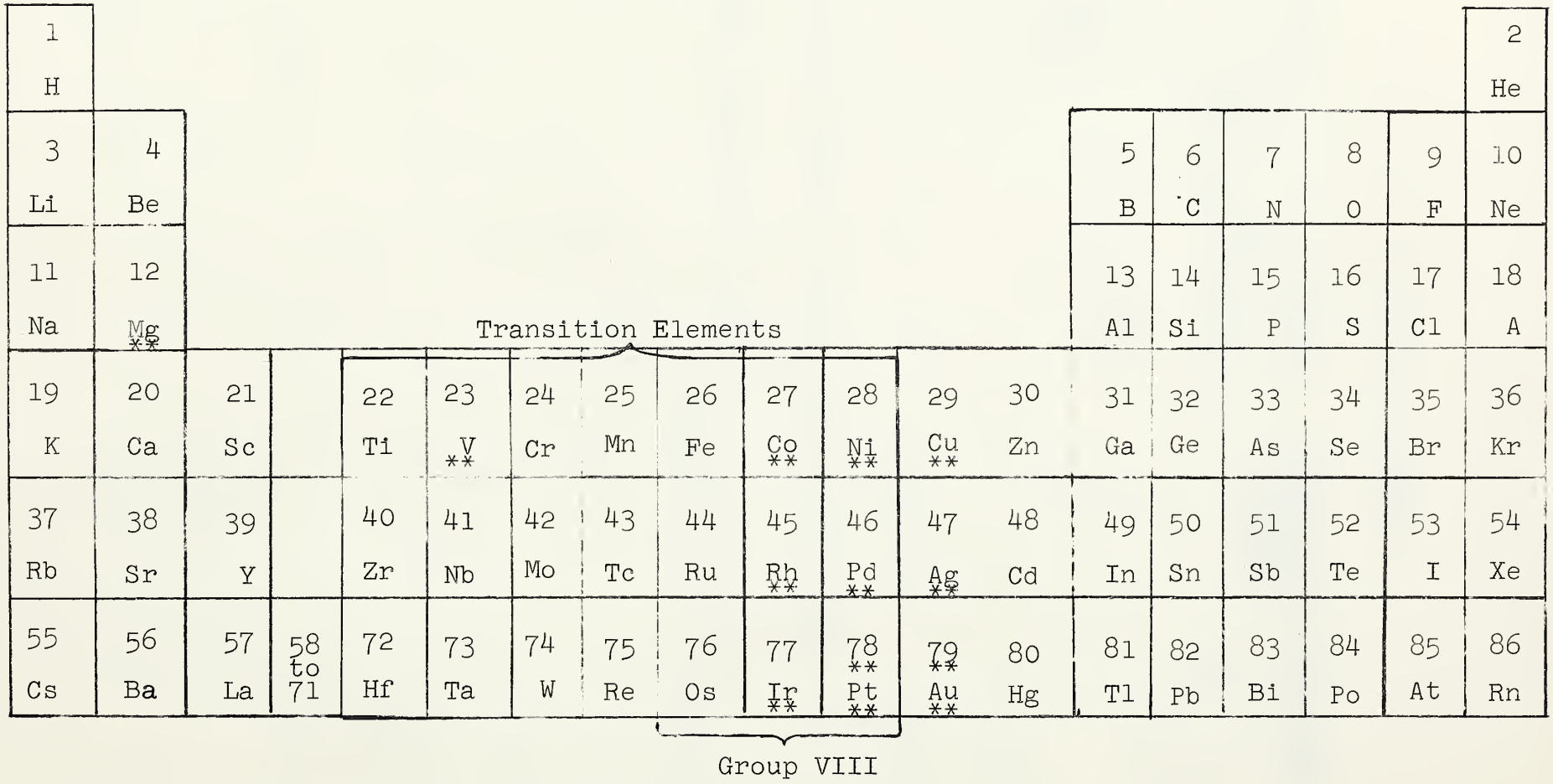
TABLE 1 (Con't.)

Alloy*	Reaction After 1 Month		X-ray	Comments
	Hardens	Does Not Harden		
Ga_E+ (35%Au65%Cu)	X		F.C.C.† +$AuGa_2$+$CuGa_2$	
Ga_E+ $Fe_{0.6}Mn_{0.4}$)		X	γFeMn (F.C.C.)	Alloy powder was not wet by the liquid Ga_E

* The abbreviation Ga_E refers to the gallium eutectic alloy with 11% tin.

? Denotes the prescence of an unidentified intermediate phase.

F.C.C.† Face-centered cubic solid solution.



** Metals which may be mixed with liquid gallium eutectic solution to produce alloys that harden at room temperature.

Figure 1

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